

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371

196389US0PCT

U.S. APPLICATION NO. IF KNOWN SEE 37 CFR

09/623487

INTERNATIONAL APPLICATION NO.

PCT/EP99/01690

INTERNATIONAL FILING DATE

15 March 1999

PRIORITY DATE CLAIMED

16 March 1998

TITLE OF INVENTION

DISPERSION RESINS CONTAINING ITACONIC ACID FOR IMPROVING WET ABRASION RESISTANCE

APPLICANT(S) FOR DO/EO/US

Cheng-Le ZHAO, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. ☒ A copy of the International Search Report (PCT/ISA/210).
8. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
9. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 18 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☒ A **FIRST** preliminary amendment.
A **SECOND** or **SUBSEQUENT** preliminary amendment.
16. ☐ A substitute specification.
17. ☐ A change of power of attorney and/or address letter.
18. ☐ Certificate of Mailing by Express Mail
19. ☒ Other items or information:

Request for Consideration of Documents Cited in International Search Report

Notice of Priority

PCT/IB/304

PCT/IB/308

Amended Sheets (Page 33 and 34)

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.53) 09/623487	INTERNATIONAL APPLICATION NO. PCT/EP99/01690	ATTORNEY'S DOCKET NUMBER 196389US0PCT
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20. The following fees are submitted:				CALCULATIONS PTO USE ONLY	
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :					
<input checked="" type="checkbox"/> Search Report has been prepared by the EPO or JPO \$840.00					
<input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) \$670.00					
<input type="checkbox"/> No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) \$760.00					
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$970.00					
<input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) \$96.00					
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$840.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).				\$0.00	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	9 - 20 =	0	x \$18.00	\$0.00	
Independent claims	1 - 3 =	0	x \$78.00	\$0.00	
Multiple Dependent Claims (check if applicable).			<input type="checkbox"/>	\$0.00	
TOTAL OF ABOVE CALCULATIONS =				\$840.00	
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable).				<input type="checkbox"/>	\$0.00
SUBTOTAL =				\$840.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).				\$0.00	
TOTAL NATIONAL FEE =				\$840.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).				<input type="checkbox"/>	\$0.00
TOTAL FEES ENCLOSED =				\$840.00	
				Amount to be refunded	\$
				charged	\$

☒ A check in the amount of **\$840.00** to cover the above fees is enclosed.

☐ Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees.
A duplicate copy of this sheet is enclosed.

☐ The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. _____ A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

<div data-bbox="243 1554 470 1638"></div> <div data-bbox="292 1638 422 1680">22850</div> <div data-bbox="503 1743 844 1827">Surinder Sachar Registration No. 34,423</div>	<div data-bbox="617 1533 812 1564">NEUSTADT, P.C.</div> <div data-bbox="925 1470 1461 1575"> SIGNATURE</div> <div data-bbox="925 1596 1461 1669">Norman F. Oblon NAME</div> <div data-bbox="925 1680 1461 1753">24,618 REGISTRATION NUMBER</div> <div data-bbox="925 1764 1461 1837">Sept 17 2000 DATE</div>
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196389US-7787-524-0 PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF :
CHENG-LE ZHAO ET AL : ATTN: APPLICATION DIVISION
SERIAL NO: NEW PCT APPLICATION :
(Based on PCT/EP99/01690)
FILED: HEREWITH :
FOR: DISPERSION RESINS :
CONTAINING ITACONIC ACID :
FOR IMPROVING WET :
ABRASION RESISTANCE :

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows:

IN THE CLAIMS

Please cancel Claims 1-8.

Please add the following claims:

--9. An emulsion paint comprising

i) a polymeric binder, which comprises at least one copolymer P of ethylenically unsaturated monomers M in the form of an aqueous polymer dispersion which has a glass transition temperature TG in the range from -10 to +50°C, and which contains in polymerized form

a) 0.1 to 1.5% by weight, based on the overall weight of the copolymer P, of itaconic acid as acidic monomer M1, its salt and/or its anhydride, it being possible for up to 50% by weight of the itaconic acid to be replaced by another monomer having at least one acid group or one neutralized acid group,

b) at least 80% by weight monomers M2, selected from vinylaromatic monomers, the esters of ethylenically unsaturated C₃-C₈ monocarboxylic acids with C₁-C₁₂-alkanols, and the vinyl esters of aliphatic C₁-C₁₂ monocarboxylic acids, and which contains no polymerized acrolein,

ii) at least one inorganic pigment,

iii) if desired, inorganic fillers/extenders, and

iv) customary auxiliaries.

10. The emulsion paint as defined in claim 9, wherein itaconic acid is the sole acidic monomer.

11. The emulsion paint as defined in claim 9, wherein the monomers M2 are selected from methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, tert-butyl methacrylate, ethyl acrylate, n-butyl acrylate, tert-butyl acrylate and 2-ethylhexyl acrylate.

12. The emulsion paint as defined in claim 9, wherein the monomers M additionally comprise from 0.1 to 10% by weight, based on the overall weight of the copolymer P, of monomers M3 comprising urea groups.

13. The emulsion paint as defined in claim 9, wherein the aqueous dispersion of the copolymer P is obtainable by free-radical aqueous emulsion polymerization of the monomers M in accordance with a monomer feed process where at least 50% by weight and in particular all of the itaconic acid is present in the monomer feed.

14. The emulsion paint as defined in claim 13, wherein the free-radical aqueous emulsion polymerization is conducted in at least two polymerization stages, where the composition of the monomers to be polymerized in the 1st stage is different from that of the monomer mixture of the monomers to be polymerized in the 2nd stage.

15. The emulsion paint as defined in claim 9, wherein the ratio of inorganic constituents to copolymer P is characterized by a pigment volume concentration $pvc > 10\%$.

16. A method of improving the wet abrasion resistance of polymer-bound coating compositions, comprising the use of a copolymer as defined in claim 9 as a binder in said coating composition.

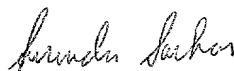
17. The method as claimed in claim 16, wherein the coating composition is an emulsion paint.--

REMARKS

Claims 9-17 are active in the present application. The claims are amended for clarity and are supported for Claims 1-10 and the specification as originally filed. No new matter has been added. Applicants submit that the present application is now in condition for examination on the merits. Early notification of such is earnestly solicited.

Respectfully submitted,

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Dispersion resins containing itaconic acid for improving wet
abrasion resistance

5 The present invention relates to pigment-comprising aqueous formulations which comprise at least one aqueous addition-polymer dispersion.

Pigmented formulations are employed widely in the form of coating
10 compositions, especially emulsion paints, synthetic-resin-bound plasters (dispersion plasters), sealing compounds or filling compositions for purposes of architectural protection or decoration. Pigmented formulations generally include as their binder a film-forming polymer, at least one inorganic pigment
15 and, if desired, one or more inorganic fillers/extenders, and customary auxiliaries. The quality of the coatings formed from pigmented formulations depends critically on the ability of the film-forming polymer to carry out uniform binding of the nonfilm-forming constituents, the pigments and the inorganic
20 fillers.

A low pigment binding capacity leads to poor mechanical stability of the coating, which is manifested, for example, in a low wet
abrasion resistance. The desire, however, is for high wet
25 abrasion resistance, especially in the case of washable emulsion paints.

The pigment binding capacity of the binder plays a particularly important part in formulations having a moderate to high content
30 of inorganic pigments and fillers/extenders. A characteristic parameter of the pigment content of a polymer-bound coating composition is the pigment volume concentration pvc. The pvc is usually defined as the percentage quotient of the overall volume of solid inorganic constituents (pigment + fillers/extenders)
35 divided by the overall volume of the solid inorganic constituents and of the polymer particles of the aqueous binder polymer dispersion; see Ullmanns Enzyklopädie der technischen Chemie, 4th edition, volume 15, p. 668.

40 In the case of exterior applications in particular, the coating compositions should be stable to environmental influences such as sunlight, moisture and fluctuations in temperature. In addition, the coating composition must adhere well to a variety of substrates even when exposed to moisture, which again depends on
45 the chosen binder polymer.

Another property dependent on the binder polymer is the blocking resistance of the coatings.

WO 93/11181 discloses titanium dioxide-containing formulations comprising, as dispersing auxiliaries, aqueous addition-polymer dispersions whose polymers include itaconic acid copolymerized in an amount of more than 1% by weight based on the weight of the addition polymer. The wet abrasion resistance of the dispersions disclosed therein leaves much to be desired.

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EP-A-810 274 discloses binders for solvent-free coating compositions which may comprise acid-functional monomers copolymerized in an amount of up to 1% by weight based on the overall weight of the monomers to be polymerized.

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The prior art binders are able to go only some of the way toward meeting the requirements that are placed on coating compositions.

It is an object of the present invention to provide pigmented formulations having a high pigment binding capacity and, therefore, high wet abrasion resistance. These properties must be ensured even at relatively high pigment volume concentrations, i.e., at pvc > 40%. The formulations should also be stable on storage - that is, their viscosity should show little or no increase even on prolonged storage.

We have found that this object is achieved by using for the formulations binders based on aqueous addition-polymer dispersions whose polymers comprise from 0.1 to 1.5% by weight of itaconic acid in copolymerized form.

The present invention accordingly provides pigment-comprising aqueous formulations comprising

- 35 i) at least one copolymer P of ethylenically unsaturated monomers M in the form of an aqueous polymer dispersion which comprises from 0.1 to 1.5% by weight, based on the overall weight of the copolymer P, of itaconic acid as acidic monomer M1, its salts and/or its anhydride in copolymerized form, it
40 being possible for up to 50% by weight of the itaconic acid to be replaced by another monomer having at least one acid group or one neutralized acid group, and has a glass transition temperature T_g in the range from -10 to +50°C,
45 ii) at least one inorganic pigment,

iii) if desired, inorganic fillers/extenders, and

iv) customary auxiliaries.

- 5 The monomers M of which the copolymer P is constructed preferably make up from 0.2 to 1.2% by weight, in particular from 0.2 to 1.0% by weight and, with particular preference, from 0.4 to 1.0% by weight. In an especially preferred embodiment the monomers M comprise from 0.5 to 0.9 and, specifically, from 0.5 to 0.8% by weight of itaconic acid as acidic monomer M1. Instead of itaconic acid it is also possible to employ its anhydride or its salts to prepare the copolymers P. A certain fraction of the itaconic acid, namely up to 50% by weight, but preferably not more than 25% by weight and in particular not more than 10% by weight, can be replaced by another monomer having at least one acid group; for example, by an ethylenically unsaturated carboxylic acid, such as acrylic acid or methacrylic acid, or by an ethylenically unsaturated sulfonic acid, an example being vinylsulfonic acid or its salts. Typical salts are the alkali metal and ammonium salts, preferably the sodium salts. Particular preference is given to employing itaconic acid as the sole acidic monomer (monomer M1).

- Normally, the preparation of the copolymers P comprising itaconic acid takes place by free-radical addition polymerization of ethylenically unsaturated monomers M which in addition to itaconic acid include at least one further comonomer. Suitable comonomers are generally selected from vinylaromatic monomers, such as styrene, α -methylstyrene, o-chlorostyrene or vinyltoluenes, the vinyl esters of aliphatic C₁-C₁₈ monocarboxylic acids, such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl valerate, vinyl hexanoate, vinyl 2-ethylhexanoate, vinyl decanoate, vinyl pivalate, vinyl laurate, vinyl stearate, and commercial monomers VEOVA® 5-11 (VEOVA® X is a tradename of Shell and stands for vinyl esters of α -branched, aliphatic carboxylic acids having X carbon atoms, which are also referred to as Versatic® X acids), and the esters of ethylenically unsaturated C₃-C₈ mono- or dicarboxylic acids with C₁-C₁₈-, preferably C₁-C₁₂- and, in particular, C₁-C₈-alkanols or C₅-C₈-cycloalkanols. Examples of suitable C₁-C₁₈-alkanols are methanol, ethanol, n-propanol, i-propanol, 1-butanol, 2-butanol, isobutanol, tert-butanol, n-hexanol, 2-ethylhexanol, lauryl alcohol and stearyl alcohol. Examples of suitable cycloalkanols are cyclopentanol and cyclohexanol. Particularly suitable esters are those of acrylic acid, methacrylic acid, crotonic acid, maleic acid, itaconic acid, citraconic acid or fumaric acid. The esters concerned are especially those of acrylic and/or methacrylic acid, such as methyl, ethyl, isopropyl, n-butyl, isobutyl,

1-hexyl, tert-butyl and 2-ethylhexyl (meth)acrylates, and also the esters of fumaric and maleic acid, examples being dimethyl fumarate, dimethyl maleate and di-n-butyl maleate. Also suitable are nitriles of α,β -monoethylenically unsaturated C_3 - C_8 carboxylic acids, such as acrylonitrile or methacrylonitrile. It is also possible, furthermore, to employ C_4 - C_8 conjugated dienes, such as 1,3-butadiene, isoprene or chloroprene, α -olefins, such as ethylene, propene and isobutene, and vinyl chloride or vinylidene chloride as comonomers.

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In addition to itaconic acid the monomers M preferably include from 50 to 99.9% by weight, based on the overall weight of the copolymer P, of at least one monomer M2 selected from the abovementioned vinylaromatic monomers, the abovementioned esters of ethylenically unsaturated C_3 - C_8 monocarboxylic acids with C_1 - C_{12} -alkanols, and the vinyl esters of aliphatic C_1 - C_{12} monocarboxylic acids. In a preferred embodiment of the present invention the monomers M2 are selected from the C_1 - C_{12} -alkyl esters of acrylic acid and C_1 - C_{12} -alkyl esters of methacrylic acid, especially methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, tert-butyl methacrylate, ethyl acrylate, n-butyl acrylate, tert-butyl acrylate and 2-ethylhexyl acrylate. Based on the overall monomer amount, the monomers M2 make up preferably at least 80% by weight and in particular at least 90% by weight. The remainder of the abovementioned comonomers (referred to below as comonomers M') are generally used in amounts < 50% by weight, preferably < 20% by weight and, in particular, < 10% by weight, based on the overall amount of the monomers M. A preferred embodiment of this invention relates to copolymers P which incorporate none of the abovementioned comonomers M'.

In a preferred embodiment of the invention the copolymers P comprise copolymerized monomers M3 which have urea groups, examples being N-vinyl- and N-allylurea and derivatives of imidazolidin-2-one, such as N-vinyl- and N-allylimidazolidin-2-one, N-vinyloxyethylimidazolidin-2-one, N-(2-(meth)acrylamidoethyl)imidazolidin-2-one, N-(2-(meth)acryloxyethyl)imidazolidin-2-one, N-[2-((meth)acryloxyacetamido)ethyl]imidazolidin-2-one etc. The monomers M3 are preferably used in amounts of from 0.1 to 10% by weight, in particular from 0.5 to 5% by weight, based on the overall weight of the copolymer P. The monomers M3 improve the wet adhesion of the coatings obtainable from the formulations of the invention, i.e., the adhesion of the coating in the wet or swollen state.

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- The copolymers P can also include in copolymerized form monomers comprising siloxane groups (monomers M4), examples being vinyltrialkoxysilanes, such as vinyltrimethoxysilane, alkylvinyl-dialkoxysilanes or (meth)acryloxyalkyltrialkoxysilanes, such as
- 5 (meth)acryloxyethyltrimethoxysilane, or (meth)acryloxypropyl-trimethoxysilane. The monomers M4 can be used in amounts of up to 1% by weight, preferably from 0.05 to 0.5% by weight, based on the overall monomer amount.
- 10 In addition, the copolymer P may also include in copolymerized form neutral or nonionic monomers M5 whose homopolymers feature increased solubility in or swellability in water. These monomers are preferably copolymerized in amounts of < 5% by weight and preferably < 2% by weight, based on the overall weight of the
- 15 copolymer P. Monomers of this kind enhance the stability of the polymer dispersions. Typical monomers M5 are the amides, the N-alkylolamides or the hydroxyalkyl esters of the abovementioned carboxylic acids, such as acrylamide, methacrylamide, N-methylol-acrylamide, N-methylolmethacrylamide, 2-hydroxyethylacrylamide,
- 20 2-hydroxyethylmethacrylamide, hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate and hydroxypropyl methacrylate.

- In preparing the copolymers P it is also possible to employ
- 25 bifunctional monomers M6. These are copolymerized if desired in minor amounts, generally from 0.1 to 5% by weight and, in particular, not more than 1% by weight, based on the overall monomer amount. Monomers M6 are preferably monomers having two nonconjugated ethylenically unsaturated bonds, examples being the
- 30 diesters of dihydric alcohols with α,β -monoethylenically unsaturated C₃-C₈ carboxylic acids, such as glycol bisacrylate, or esters of α,β -unsaturated carboxylic acids with alkenols, such as bicyclodecenyl (meth)acrylate. Preferred polymers P contain no copolymerized monomers M6.

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- The character of the formulations of the invention is also dependent on the glass transition temperature (DSC, midpoint temperature, ASTM D 3418-82) of the copolymer P. If the glass transition temperature is too low, the coating is not very strong
- 40 and tears when subjected to a mechanical load. If it is too high, the polymer no longer forms a film and the coating, consequently, is of reduced wet abrasion resistance. The glass transition temperature of the copolymers P in question is therefore below 50°C and preferably below 40°C, in particular below 30°C. In
- 45 general, however, it is above -10°C. It proves useful in this context to estimate the glass transition temperature T_g of the dispersed polymer. According to Fox (T.G. Fox, Bull. Am. Phys.

Soc. (Ser. II) 1, [1956] 123 and Ullmanns Enzyklopädie der technischen Chemie, Weinheim (1980), p. 17, 18) the glass transition temperature of copolymers at high molar masses is given in good approximation by

$$\frac{1}{T_g} = \frac{X^1}{T_g^1} + \frac{X^2}{T_g^2} + \dots + \frac{X^n}{T_g^n}$$

where X^1, X^2, \dots, X^n are the mass fractions of the monomers 1, 2, ..., n and $T_g^1, T_g^2, \dots, T_g^n$ the glass transition temperatures of the homopolymers of 1, 2, ..., n, in kelvins. The latter are known, for example, from Ullmann's Encyclopedia of Industrial Chemistry, VCH, Weinheim, Vol. A 21 (1992) p. 169 or from J. Brandrup, E.H. Immergut, Polymer Handbook 3rd ed., J. Wiley, New York 1989.

From what has been said above it is clear that the glass transition temperature of the copolymer P can be adjusted both by choosing an appropriate principal monomer M2, having a glass transition temperature within the desired range, and by combining at least one monomer M2a having a high glass transition temperature with at least one monomer M2b having a low glass transition temperature, the latter procedure being preferred.

In a preferred embodiment of the present invention the monomers M making up the copolymer P include at least one monomer M2a whose homopolymer, for the limiting case of a very high (infinite) molecular mass, has a glass transition temperature $T_g > 30^\circ\text{C}$ and at least one monomer M2b, whose homopolymer has a glass transition temperature $T_g < 20^\circ\text{C}$. Examples of monomers M2a suitable for this purpose are styrene, α -methylstyrene, methyl methacrylate, ethyl methacrylate, n- and iso-propyl methacrylate, n-, iso- and tert-butyl methacrylate, tert-butyl acrylate and vinyl acetate, and also acrylonitrile and methacrylonitrile, the two nitriles preferably accounting for not more than 30% by weight of the monomers M2a. Examples of monomers M2b suitable for this purpose are the C_1 - C_{12} -alkyl acrylates, butadiene, vinyl versatates, and especially ethyl acrylate, n-butyl acrylate and 2-ethylhexyl acrylate. Particular preference is given to monomer combinations M2a/M2b which comprise styrene and/or methyl methacrylate and also n-butyl acrylate with or without 2-ethylhexyl acrylate.

In one particularly preferred embodiment of the present invention the copolymer P is constructed from:

- i) from 20 to 80% by weight, preferably from 35 to 70% by weight, of monomers M2a, especially styrene and/or methyl methacrylate, specifically methyl methacrylate as sole monomer M2a,

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- ii) from 20 to 79.7% by weight, preferably from 30 to 65% by weight, of monomers M2b, especially n-butyl acrylate and/or ethylhexyl acrylate,

- 10 iii) from 0.1 to 1.5% by weight, preferably from 0.2 to 1.2% by weight, especially from 0.3 to 1.0% by weight and, with particular preference, from 0.5 to 0.8% by weight of itaconic acid,

- 15 iv) from 0.2 to 5% by weight, preferably from 0.5 to 3% by weight of monomers M3 having at least one urea group, especially an ethylenically unsaturated derivative of imidazolidin-2-one,

where the proportions by weight of the monomers M1, M2a, M2b and
20 M3 add up to 100% by weight. Such copolymers P are frequently employed in formulations of the invention comprising solvents.

In another preferred embodiment of the present invention the copolymer P is constructed from:

25

- i) from 20 to 69.7% by weight, preferably from 30 to 60% by weight, of monomers M2a, especially styrene and/or methyl methacrylate, specifically styrene as sole monomer M2a,

- 30 ii) from 30 to 80% by weight, preferably from 40 to 70% by weight, of monomers M2b, especially n-butyl acrylate and/or ethylhexyl acrylate,

- iii) from 0.2 to 1% by weight, preferably from 0.4 to 0.9% by
35 weight, especially from 0.5 to 0.8% by weight of itaconic acid,

- iv) from 0.1 to 3% by weight, in particular from 0.2 to 2% by weight, of monomers M5, especially acrylamide and/or

40

methacrylamide,

where the proportions by weight of the monomers M1, M2a, M2b and M5b add up to 100% by weight. Such copolymers P are frequently employed in formulations of the invention that are solvent-free.

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The copolymers P of the two preferred embodiments can of course be modified with siloxane groups, by means, for example, of copolymerized monomers M4 (see above) or by using regulators containing siloxane groups, examples being mercaptoalkyltri-
5 alkoxy silanes such as mercaptopropyltrimethoxysilane.

It has additionally proven advantageous if the polymer particles in the binder polymer dispersion have a ponderal median polymer particle diameter in the range from 50 to 1000 nm (determined by
10 means of an ultracentrifuge or by photon correlation spectroscopy; regarding the determination of particle size by means of an ultra-centrifuge see, for example, W. Mächtle, Makromolekulare Chemie 185, (1984) 1025-1039 and W. Mächtle, Angew. Makromolekulare Chemie 162 (1988) 35-42). In the case of binder
15 dispersions with high solids contents, such as > 50% by weight, based on the overall weight of the binder dispersion, it is advantageous on grounds of viscosity for the ponderal median diameter of the polymer particles in the dispersion to be \geq 250 nm. The median particle diameter will generally not exceed 1000
20 nm and preferably will not exceed 600 nm.

The aqueous polymer dispersions employed in accordance with the invention are preferably prepared by free-radical aqueous emulsion polymerization of the abovementioned monomers in the
25 presence of at least one free-radical polymerization initiator and, if desired, of a surface-active substance.

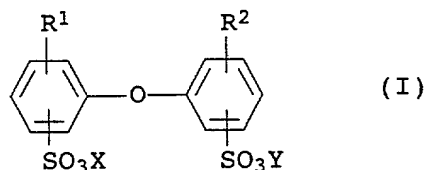
Suitable free-radical polymerization initiators are all those capable of triggering a free-radical aqueous emulsion poly-
30 merization reaction. They can be peroxides, for example, alkali metal peroxodisulfates, or azo compounds. As polymerization initiators it is common to use redox initiators, which are composed of at least one organic reducing agent and at least one peroxide and/or hydroperoxide, examples being tert-butyl
35 hydroperoxide with sulfur compounds, such as the sodium salt of hydroxymethanesulfinic acid, sodium sulfite, sodium disulfite, sodium thiosulfate or acetone bisulfite adduct, or hydrogen peroxide with ascorbic acid. Use is also made of combined systems which comprise a small amount of a metal compound which is
40 soluble in the polymerization medium and whose metal component can exist in a plurality of valence states, an example of such a system being ascorbic acid/iron(II) sulfate/hydrogen peroxide, where the ascorbic acid is frequently replaced by the sodium salt of hydroxymethanesulfinic acid, acetone bisulfite adduct, sodium
45 sulfite, sodium hydrogen sulfite or sodium bisulfite, and the hydrogen peroxide by organic peroxides, such as tert-butyl hydroperoxide, or alkali metal peroxodisulfates and/or ammonium

peroxodisulfate. Initiators which are likewise preferred are peroxodisulfates, such as sodium peroxodisulfate. The amount of the free-radical initiator system that is employed, based on the overall amount of monomers to be polymerized, is preferably from 5 0.1 to 2% by weight.

Surface-active substances suitable for conducting the emulsion polymerization are the emulsifiers and protective colloids commonly employed for this purpose. The surface-active substances 10 are normally employed in amounts of up to 10% by weight, preferably from 0.5 to 5% by weight and, in particular, from 1 to 4% by weight, based on the monomers to be polymerized.

Examples of suitable protective colloids are polyvinyl alcohols, 15 starch derivatives and cellulose derivatives, or vinylpyrrolidone copolymers. An exhaustive description of further suitable protective colloids is given in Houben-Weyl, Methoden der organischen Chemie, Volume XIV/1, Makromolekulare Stoffe [Macromolecular substances], Georg-Thieme-Verlag, Stuttgart 1961, 20 pp. 411-420.

As surface-active substances it is preferred to employ exclusively emulsifiers, whose relative molecular weights, unlike those of the protective colloids, are usually below 2000. They 25 can be anionic or nonionic in nature. The anionic emulsifiers include alkali metal salts and ammonium salts of alkyl sulfates (alkyl: C₈-C₁₂), of sulfuric monoesters with ethoxylated alkanols (EO units: 2 to 50, alkyl: C₁₂ to C₁₈) and with ethoxylated alkylphenols (EO units: 3 to 50, alkyl: C₄-C₉), of alkylsulfonic 30 acids (alkyl: C₁₂-C₁₈) and of alkylarylsulfonic acids (alkyl: C₉ to C₁₈), and also compounds of the general formula I,



35

where R¹ and R² are hydrogen or C₄-C₂₄-alkyl, preferably C₈-C₁₆-alkyl, but are not both hydrogen and X and Y can be alkali 40 metal ions and/or ammonium ions. Use is frequently made of technical-grade mixtures which have a proportion of from 50 to 90% by weight of the monoalkylated product, an example being Dowfax® 2A1 (R¹ = C₁₂-alkyl; DOW CHEMICAL). The compounds I are widely known, from US-A-4,269,749, for example, and are 45 obtainable commercially.

- Suitable nonionic emulsifiers are araliphatic or aliphatic nonionic emulsifiers, examples being ethoxylated mono-, di- and trialkylphenols (EO units: 3 to 50, alkyl: C₄-C₉), ethoxylates of long-chain alcohols (EO units: 3 to 50, alkyl: C₈-C₃₆), and
- 5 polyethylene oxide/polypropylene oxide block copolymers. Preference is given to ethoxylates of long-chain alkanols (alkyl: C₁₀-C₂₂, average degree of ethoxylation: 3 to 50) and, of these, particular preference to those based on naturally occurring alcohols or on oxo alcohols having a linear or branched
- 10 C₁₂-C₁₈-alkyl radical and a degree of ethoxylation of from 8 to 50. Preference is given to anionic emulsifiers or to combinations of at least one anionic and one nonionic emulsifier.

Further suitable emulsifiers are given in Houben-Weyl, op. cit.
15 pp. 192-208.

- The molecular weight of the copolymers P can be adjusted by adding small amounts, generally up to 2% by weight based on the monomers to be polymerized, of one or more molecular weight
- 20 regulators, examples being organic thiocompounds, silanes, allyl alcohols, and aldehydes.

- The emulsion polymerization can be conducted either continuously or by the batch procedure, preferably by a semicontinuous
- 25 process. In semicontinuous processes the major amount - that is, at least 70%, preferably at least 90% of the monomers to be polymerized - is supplied continuously, including by a staged or gradient procedure, to the polymerization batch. This procedure is also referred to as the monomer feed process. It has been
- 30 found advantageous in this context for the major amount of the itaconic acid - that is, at least 50%, preferably at least 80%, in particular at least 90% and, with very particular preference, all of the itaconic acid to be supplied to the polymerization reaction by way of the monomer feed; in other words, no more than
- 35 50% of the itaconic acid and, with very particular preference, no itaconic acid is included in the initial charge to the polymerization vessel before the polymerization is begun. By monomer feeds are meant liquid monomer mixtures, monomer solutions or, in particular, aqueous monomer emulsions.

40

- In addition to the seed-free preparation method it is also possible, in order to establish a defined polymer particle size, to conduct the emulsion polymerization by the seed latex process or in the presence of a seed latex prepared in situ. Processes
- 45 for this purpose are known and can be found in the prior art (see EP-B 40419, EP-A-614 922, EP-A-567 812 and literature cited therein and also 'Encyclopedia of Polymer Science and

Technology', Vol. 5, John Wiley & Sons Inc., New York 1966, p. 847).

The polymerization is preferably conducted in the presence of
5 from 0.01 to 3% by weight and, in particular, from 0.02 to 1.5% by weight of a seed latex (solids content of the seed latex, based on overall monomer amount), preferably with a seed latex included in the initial charge (initial charge seed).

- 10 The preparation of the aqueous dispersions of the copolymers P can also be carried out by what is known as staged polymerization. This means a procedure in a 1st stage of which the monomers of the 1st stage are polymerized by free-radical aqueous emulsion polymerization, preferably in the presence of a
15 seed latex, after which the monomers of the 2nd stage are polymerized in the aqueous dispersion of the resultant 1st-stage polymer. This may be followed by further polymerization stages. In such a procedure, the monomer mixtures of the 1st stage and of the 2nd stage differ in the nature of the monomers and/or in the
20 relative proportions of the monomers. The nature of the monomers to be polymerized in the 1st and 2nd stages is preferably the same. Where the monomers M include both a monomer M2a and a monomer M2b, the monomer mixtures of the 1st stage differ from those of the 2nd stage by the proportion M2a/M2b. In particular,
25 the proportion M2a/M2b in the 1st stage is greater than the proportion M2a/M2b in the 2nd stage. The proportion of the monomers of the 1st stage to the monomers of the 2nd stage lies preferably within the range from 1:10 to 10:1 and, in particular, in the range from 1:5 to 5:1. Staged polymerization achieves the
30 polymerization of the monomers of the 2nd stage (and, where appropriate, of subsequent stages) onto the polymer particles of the 1st stage.

- The pressure and temperature of polymerization are of minor
35 importance. It is normal to operate at temperatures of between room temperature and 120°C, preferably at temperatures from 40 to 95°C and, with particular preference, between 50 and 90°C.

- Following the polymerization reaction proper, it may be necessary
40 to render the aqueous polymer dispersions of the invention substantially free from odoriferous substances, such as residual monomers and other volatile organic constituents. This can be done physically in a manner known per se, by distillative removal (especially by steam distillation), or by stripping with an inert
45 gas. The residual monomer content can also be lowered chemically by means of free-radical postpolymerization, especially under the action of redox initiator systems, as are set out, for example,

in DE-A 44 35 423. Postpolymerization is preferably conducted with a redox initiator system comprising at least one organic peroxide and one organic sulfite.

- 5 The dispersions of the copolymer P are preferably adjusted to a pH in the range from 6 to 10 before being used in the formulations of the invention, preferably by adding a nonvolatile base, examples being alkali metal hydroxides, alkaline earth metal hydroxides or nonvolatile amines.

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By the method of emulsion polymerization it is possible in principle to obtain dispersions having solids contents of up to about 80% by weight (polymer content based on the overall weight of the dispersion). For practical reasons it is generally

- 15 preferred to use polymer dispersions having solids contents in the range from 40 to 70% by weight for the formulations of the invention. Particular preference is given to dispersions having polymer contents of about 50% by weight. Dispersions having lower solids contents are of course suitable in principle for use for
20 the formulations of the invention.

In accordance with the invention the copolymers P comprising itaconic acid are employed in the form of their aqueous polymer dispersions as binders in pigmented formulations that are used to
25 coat substrates. Examples of what are meant by such formulations include polymer dispersion plasters, tile adhesives, paints and varnishes, and sealants or sealing compounds, especially for porous components.

- 30 A preferred embodiment of the present invention relates to formulations in the form of emulsion paints.

- The formulations of the invention, preferably emulsion paints, generally contain from 30 to 75% by weight and, preferably, from
35 40 to 65% by weight, of nonvolatile constituents. By these are meant all those constituents of the formulation except for water, but at least the total amount of binder, extender, pigment, solvents of low volatility (boiling point above 220°C), such as plasticizers, and polymeric auxiliaries. Of these, the amounts
40 accounted for by each class of constituent are

- i from 3 to 90% by weight, preferably from 10 to 60% by weight, by solid binder constituents (= copolymer P),
- 45 ii from 5 to 85% by weight, preferably from 10 to 60% by weight, by at least one inorganic pigment,

iii from 0 to 85% by weight, preferably from 20 to 70% by weight, by inorganic fillers, and

- iv from 0.1 to 40% by weight, preferably from 0.5 to 15% by weight, by customary auxiliaries.
- 5

The pvc of the formulations is generally above 10%, for example from 15 to 85%. In one preferred embodiment of the invention it is within the range from 15 to 25%. In another preferred

- 10 embodiment of the invention the pvc is in the range from > 40% to 60% by weight, e.g., at about 45% by weight. In a further preferred embodiment of the invention the pvc is > 60%, preferably > 70%, and can be up to 85%.

- 15 Typical pigments for the formulations of the invention, especially for emulsion paints, are, for example, titanium dioxide, preferably in the rutile form, barium sulfate, zinc oxide, zinc sulfide, basic lead carbonate, antimony trioxide, and lithopones (zinc sulfide + barium sulfate). However, the
- 20 formulations may also comprise color pigments, examples being iron oxides, carbon black, graphite, luminescent pigments, zinc yellow, zinc green, ultramarine, manganese black, antimony black, manganese violet, Paris blue or Schweinfurt green. In addition to the inorganic pigments the formulations of the invention may also
- 25 include organic color pigments, examples being sepia, gamboge, Cassel brown, toluidine red, para red, Hansa yellow, indigo, azo dyes, anthraquinonoid and indigoid dyes, and also dioxazine, quinacridone, phthalocyanine, isoindolinone and metal complex pigments.

- 30 Suitable fillers include, in principle, aluminosilicates, such as feldspars, silicates, such as kaolin, talc, mica, magnesite, alkaline earth metal carbonates, such as calcium carbonate, in the form, for example, of calcite or chalk, magnesium carbonate,
- 35 dolomite, alkaline earth metal sulfates, such as calcium sulfate, silicon dioxide, etc. The fillers can be employed as individual components. In practice, however, filler mixtures have proven especially suitable, such as calcium carbonate/kaolin and calcium carbonate/talc. Dispersion plasters may also include relatively
- 40 coarse aggregates, such as sands or sandstone granules. In emulsion paints, of course, finely divided fillers are preferred.

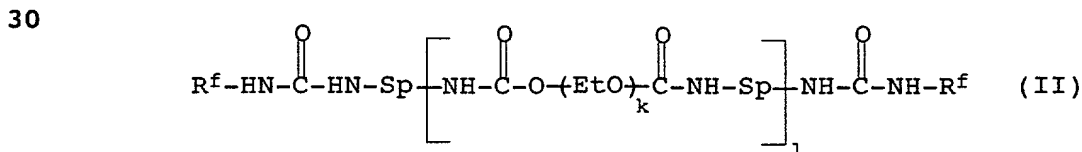
- To increase the hiding power and to save on the use of white pigments it is common in the preferred emulsion paints to employ
- 45 finely divided fillers (extenders), examples being finely divided calcium carbonate or mixtures of different calcium carbonates having different particle sizes. To adjust the hiding power, the

shade and the depth of color it is preferred to employ blends of color pigments and extenders.

- The customary auxiliaries iv include wetting agents or
 5 dispersants, such as sodium, potassium or ammonium polyphosphates, alkali metal salts and ammonium salts of polyacrylic acids and of polymaleic acid, polyphosphonates, such as sodium 1-hydroxyethane-1,1-diphosphonate, and salts of naphthalenesulfonic acids, especially their sodium salts. The
 10 dispersants are generally employed in an amount of from 0.1 to 0.6% by weight based on the overall weight of the emulsion paint.

- The auxiliaries iv may also include thickeners, examples being cellulose derivatives, such as methylcellulose, hydroxyethyl-
 15 cellulose and carboxymethylcellulose, and also casein, gum arabic, tragacanth gum, starch, sodium alginate, polyvinyl alcohol, polyvinylpyrrolidone, sodium polyacrylates, water-soluble copolymers based on acrylic and methacrylic acid, such as acrylic acid-acrylamide and methacrylic acid-acrylate copolymers,
 20 and what are known as associative thickeners, examples being styrene-maleic anhydride polymers or, preferably, hydrophobically modified polyetherurethanes, as are described, for example, by N. Chen et al. in J. Coatings Techn. Vol 69, No. 867, 1997, p. 73 and by R. D. Hester et al. in J. Coatings Technology, Vol. 69,
 25 No. 864, 1997, 109, the content of which is hereby incorporated in its entirety by reference.

Examples of hydrophobically modified polyetherurethanes are polymers of the general formula II



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- where R^f is a hydrophobic radical, preferably a linear or branched alkyl of 10 to 20 carbon atoms, Et is 1,2-ethylene, Sp is $\text{C}_2\text{-C}_{10}$ -alkylene, cycloalkylene or arylene, k is from 50 to 1000
 40 and l is from 1 to 10, the product $k \times l$ preferably being from 300 to 1000. The dispersants and/or wetting agents are employed in general in an amount of from 0.1 to 0.6% by weight, based on the overall weight of the emulsion paint.
- 45 Inorganic thickeners, such as bentonites or hectorite, can also be used. Thickeners are generally used in amounts of from 0.1 to 3% by weight, preferably from 0.1 to 1% by weight, based on the

overall weight of the aqueous formulation. In addition, the auxiliaries iv generally also include defoamers, preservatives or hydrophobicizing agents, biocides, fibers or other constituents.

- 5 In addition, in order to adjust the film-forming properties of the binder polymers, the coating compositions may also comprise what are known as film-forming consolidating agents (plasticizers), examples being ethylene glycol, propylene glycol, butylene glycol, hexylene glycol, alkyl ethers and alkyl ether
- 10 esters of glycols and polyglycols, e.g., diethylene glycol monoethyl ether, diethylene glycol monoethyl ether acetate, diethylene glycol monobutyl ether, hexylene glycol diacetate, propylene glycol monoethyl ether, monophenyl ether, monobutyl ether and monopropyl ether, dipropylene glycol monomethyl ether,
- 15 and mono-n-butyl ether, tripropylene glycol mono-n-butyl ether, and the acetates of said monoalkyl ethers, such as butoxybutyl acetate, and also alkyl esters of aliphatic mono- and dicarboxylic acids, such as Texanol[®] from Eastman, or technical-grade mixtures of dibutyl esters of succinic, glutaric
- 20 and adipic acid. Film-forming auxiliaries are customarily employed in amounts of from 0.1 to 20% by weight, based on the copolymer P present in the formulation, so that the formulation has a minimum film-forming temperature of $< 15^{\circ}\text{C}$ and preferably in the range from 0 to 10°C .
- 25 A distinction is often made between solventborne and solventless paints. Solventborne paints are preferably employed for exterior applications and solventless paints preferably for interior applications. Typical solventborne paints include not only the
- 30 abovementioned film-forming auxiliaries but also, for the same purpose, hydrocarbons and/or mixtures thereof, with or without aromatic constituents, such as white spirits in the boiling range from 140 to 210°C . The copolymers P in solventborne formulations often have a glass transition temperature $T_g \geq 5^{\circ}\text{C}$ and,
- 35 preferably, $\leq 30^{\circ}\text{C}$. In solventless paints the glass transition temperature is preferably $\leq 10^{\circ}\text{C}$.

- Furthermore, the formulations employed in accordance with the invention may also include crosslinking additives. Additives of
- 40 this kind can be aromatic ketones, such as alkyl phenyl ketones unsubstituted or with one or more substituents on the phenyl ring, or benzophenone and substituted benzophenones, as photoinitiators. Photoinitiators suitable for this purpose are known, for example, from DE-A-38 27 975 and EP-A-417 568. Other
- 45 suitable crosslinking compounds are water-soluble compounds having at least two amino groups, examples being dihydrazides of aliphatic dicarboxylic acids in accordance with DE-A-39 01 073,

if the copolymer P comprises carbonyl-containing monomers in copolymerized form.

- The formulations of the invention are stable fluid systems which can be used to coat a large number of substrates. Accordingly, the present invention also provides a method of coating substrates. Examples of suitable substrates are wood, concrete, metal, glass, ceramics, plastic, plaster, wallpaper and coated, primed or weathered substrates. The formulation is applied to the target substrate in a manner dependent on the form of the formulation. Depending on the viscosity and pigment content of the formulation and on the substrate, application may take place by means of rolling, brushing, knife coating or spraying.
- 15 The coatings produced using the formulations of the invention are notable for high wet abrasion resistance and good adhesion under damp conditions, i.e., in the wet or swollen state. An improved wet abrasion resistance - in other words, an improved mechanical stability of the coatings toward abrasive influences in the damp state - is favorable for the weathering stability and wet cleaning stability of the coatings and therefore means that they can be washed. Moreover, the coatings are not tacky, and feature high blocking resistance.
- 25 The advantageous properties of the copolymer P as binder relative to prior art binder polymers, and especially its improved wet abrasion resistance, is equally in evidence in the case of pigmented formulations having a pvc of < 40% and in the case of formulations having a pvc of > 40% or a pvc of > 60%. The advantages of the invention become particularly evident if the formulations have a pvc of > 40% and up to 85%, for example, a pvc of about 45% or a pvc of from 70 to 80%. Accordingly, the present invention also provides for the use of the copolymers P to improve the wet abrasion resistance of pigment-comprising formulations.

The examples below are intended to illustrate the invention without restricting it.

- 40 I. Preparing and characterizing the polymer dispersions (Copolymers P)

- The average particle size (z-average) of the polymer particles was found by dynamic light scattering (photon correlation spectroscopy) on a 0.01% by weight dispersion in water at 23°C using an Autosizer IIc from Malvern

Instruments, England. The value stated is the cumulant z-average of the measured autocorrelation function.

5 The minimum film-forming temperature (MFT) of the polymer
dispersions was determined in accordance with Ullmanns
Enzyklopädie der technischen Chemie, 4th ed., Vol. 19, VCH
Weinheim 1980, p. 17. The measuring device used was a film
formation bench (a metal plate to which a temperature
10 gradient is applied and on which temperature sensors are
mounted at different points for the purpose of temperature
calibration, the temperature gradient being chosen such that
one end of the film formation bench has a temperature above
the anticipated MFT and the other end has a temperature below
the anticipated MFT). The aqueous polymer dispersion is then
15 applied to the film formation bench. In those regions of the
film formation bench whose temperature is above the MFT the
dispersion dries to form a clear film whereas in the cooler
regions cracks appear in the film and at lower temperatures
still it forms a white powder. The MFT is determined visually
20 on the basis of the known temperature profile of the plate.

1. Comparative dispersion CD1

25 A reactor was charged with 234 g of deionized water, 38 g
of aqueous sodium pyrophosphate solution (5% strength by
weight) and 4.61 g of a polystyrene seed latex (particle
size about 30 nm, solids content about 33% by weight).
This initial charge was heated to 85°C under nitrogen.
Then 7.24 g of aqueous initiator solution were added. A
30 monomer emulsion was then added over the course of 3
hours, and the remainder of the initiator solution over
the course of 4 hours. After the end of the addition of
initiator the temperature was maintained for 1 hour and
then lowered to 60°C. Subsequently, 6.36 g of a 15%
35 strength by weight aqueous solution of tert-butyl hydro-
peroxide and 7.25 g of an aqueous 13.1% strength by
weight solution of acetone bisulfite were supplied to the
reactor by way of separate feeds. The 60°C were
maintained for 1 hour. The batch was then cooled to room
40 temperature and its pH adjusted to 7.4 using 10% strength
by weight sodium hydroxide solution. The resulting
dispersion was free from coagulum and had a solids
content of 60.1% by weight. The ponderal median particle
diameter of the polymer was 270 nm. Its MFT was 6°C.

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Initiator solution: 2.38 g of sodium peroxodisulfate
70.00 g of deionized water

5 Monomer emulsion: 227.73 g of deionized water
21.11 g of emulsifier solution 1
47.50 g of emulsifier solution 2
356.25 g of methyl methacrylate
502.55 g of n-butyl acrylate
19.00 g of methacrylic acid
10 72.20 g of a 25% strength by weight solution of N-(methacryloxyethyl)imidazolidin-2-one in methyl methacrylate

15 Emulsifier solution 1: 45% strength by weight solution of sodium (dodecylsulfonylphenoxy)benzenesulfonate (Dowfax® 2A1 from Dow Chemicals) in water

20 Emulsifier solution 2: 30% strength by weight solution of the sodium salt of a sulfuric monoester mixture of C₁₀-C₁₆-alkyl ethoxylates (average EO units 30) in water (Disponil® FES 77 from Henkel KGaA).
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2. Comparative dispersion CD2

30 In the manner described for CD1 but with a different monomer composition a comparative dispersion CD2 was prepared. Instead of the polystyrene seed latex the initial charge contained 19 g of acrylate latex (50% strength by weight, $d_{50} = 130$ nm). Following the polymerization reaction, the pH was adjusted to 7.0 using 10%
35 strength by weight sodium hydroxide solution. The resulting dispersion was free from coagulum and had a solids content of 58.7% by weight. The average diameter of the polymer particles was 235 nm. The MFT was 4°C.

40 Monomer emulsion: 226.41 g of water
21.11 g of emulsifier solution 1
47.50 g of emulsifier solution 2
356.25 g of methyl methacrylate
502.55 g of n-butyl acrylate
45 19.00 g of itaconic acid

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72.20 g of a 25% strength by weight solution of N-(methacryloxyethyl)imidazolidin-2-one in methyl methacrylate.

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3. Comparative dispersion CD3

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A reactor was charged with 175 g of deionized water, 38 g of aqueous sodium pyrophosphate solution (5% strength by weight) and 3.80 g of a polystyrene seed latex (particle size about 30 nm, solids content about 5% by weight). This initial charge was heated to 85°C under nitrogen. Then 7.24 g of aqueous initiator solution were added. A monomer emulsion was then added over the course of 3 hours, and the remainder of the initiator solution over the course of 4 hours. After the end of the addition of initiator the temperature was maintained for 1 hour and then lowered to 60°C. Subsequently, 1.36 g of a 15% strength by weight aqueous solution of tert-butyl hydroperoxide and 7.25 g of an aqueous 13.1% strength by weight solution of acetone bisulfite were supplied to the reactor by way of separate feeds. The 60°C were maintained for 1 hour. The batch had its pH adjusted to 8.5 using 10% strength by weight sodium hydroxide solution. The resulting dispersion was free from coagulum and had a solids content of 52.8% by weight. The ponderal median particle diameter was 280 nm. Its MFT was 2°C.

Initiator solution: 2.38 g of sodium peroxodisulfate
 70.00 g of deionized water

Monomer emulsion: 379.15 g of deionized water
 63.33 g of emulsifier solution 3
 118.75 g of emulsifier solution 4
 391.88 g of methyl methacrylate
 513.00 g of n-butyl acrylate
 19.00 g of itaconic acid
 38.00 g of a 25% strength by weight solution of N-(methacryloxyethyl)imidazolidin-2-one in methyl methacrylate.

Emulsifier solution 3: 15% strength by weight solution of sodium dodecylbenzenesulfonate in water

Emulsifier solution 4: 20% strength by weight solution of an ethoxylated C₁₆-C₁₈ fatty alcohol (18 EO units)

5 4. Comparative dispersion CD4

10 A polymerization reactor was charged with 235 g of deionized water and 3.8 g of polystyrene seed latex (5% strength by weight, $d_{50} = 30$ nm) and this initial charge was flushed with nitrogen and heated to 85°C. Then 7.24 g of aqueous initiator solution were added. Subsequently, still at 85°C, the monomer emulsion I was added over the course of 3 h and the initiator solution over the course of 4 h. After the end of the addition of the monomer emulsion I the monomer emulsion II was introduced into the reactor over the course of 1 h. After the end of the addition of initiator and monomer the 85°C were maintained for a further hour and the batch was then cooled to 60°C. Then, at 60°C, 1.36 g of a 15% strength by weight aqueous solution of tert-butyl hydroperoxide and 7.25 g of a 13.1% strength by weight aqueous solution of acetone bisulfite were introduced into the reactor by way of separate feeds and the 60°C were maintained for 1 hour. The batch was then cooled to room temperature and its pH was adjusted to 8.5 using 10% strength by weight sodium hydroxide solution. The dispersion was free from coagulum and had a solids content of 63.9% by weight. The average polymer particle diameter was 270 nm and the minimum film-forming temperature of the dispersion was 13°C.

Initiator solution: 2.38 g of sodium peroxodisulfate
70.00 g of deionized water
Monomer emulsion I: 47.84 g of deionized water
35 66.50 g of emulsifier solution 3
(see CD3)
66.50 g of emulsifier solution 4
(see CD3)
14.25 g of 10% strength by weight
40 sodium hydroxide solution
332.03 g of methyl methacrylate
312.55 g of n-butyl acrylate
4.75 g of acrylic acid

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9.75 g of a 25% strength by weight solution of N-(methacryloxyethyl)-imidazolidin-2-one in methyl methacrylate

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Monomer emulsion II: 16.98 g of deionized water
28.50 g of emulsifier solution 3
28.50 g of emulsifier solution 4
108.20 g of methyl methacrylate
140.41 g of n-butyl acrylate
2.38 g of acrylic acid
28.50 g of a 25% strength by weight solution of N-(methacryloxyethyl)imidazolidin-2-one in methyl methacrylate

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5. Comparative dispersion CD5

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CD5 was prepared in analogy to CD4 but replacing the acrylic acid by equal amounts of methacrylic acid. Following the polymerization, the pH was adjusted to 8.6. The dispersion was free from coagulum and had a solids content of 62.8% by weight. The ponderal median polymer particle diameter was 272 nm and the minimum film-forming temperature was 10°C.

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6. Dispersion D1 (inventive)

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The inventive dispersion D1 was prepared in analogy to the comparative dispersion CD3. The monomer emulsion had the following composition:

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117.74 g of deionized water
63.33 g of emulsifier solution 3
118.75 g of emulsifier solution 4
391.88 g of methyl methacrylate
513.00 g of n-butyl acrylate
9.50 g of itaconic acid
38.00 g of a 25% strength by weight solution of N-(methacryloxyethyl)imidazolidin-2-one in methyl methacrylate

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Following its preparation, the pH of the dispersion was adjusted to 8.7 using 10% strength by weight sodium hydroxide solution. The resulting dispersion was free from coagulum and had a solids content of 62.8% by

weight. The ponderal median polymer particle diameter was 311 nm, the MFT 4.0°C.

7. Dispersion D2

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The inventive dispersion D2 was prepared in analogy to the comparative dispersion CD2.

The monomer emulsion had the following composition:

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230.96 g of deionized water
21.11 g of emulsifier solution 1 (see CD1)
47.50 g of emulsifier solution 2 (see CD1)
356.25 g of methyl methacrylate
15 502.55 g of n-butyl acrylate
9.50 g of itaconic acid
72.20 g of 25% strength by weight solution of N-(methacryloxyethyl)imidazolidin-2-one in methyl methacrylate

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Following the polymerization the dispersion was neutralized to a pH of 7.0 with 10% strength by weight sodium hydroxide solution. The resulting dispersion was virtually free from coagulum and had a solids content of 25 58.7% by weight. The average polymer particle diameter was 235 nm, the MFT was 4.0°C.

8. Dispersion D3

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The inventive dispersion D3 was prepared in analogy to the comparative dispersion CD3. The monomer emulsion had the following composition:

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92.62 g of deionized water
63.33 g of emulsifier solution 3 (see CD3)
118.75 g of emulsifier solution 4 (see CD3)
391.88 g of methyl methacrylate
513.00 g of n-butyl acrylate
7.13 g of itaconic acid
40 38.00 g of a 25% strength by weight solution of N-(methacryloxyethyl)imidazolidin-2-one in methyl methacrylate

45

The dispersion was neutralized to a pH of 9.5 with 10% strength by weight sodium hydroxide solution. The resulting dispersion was free from coagulum and had a

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solids content of 64.9% by weight. The average polymer particle diameter was 285 nm, the MFT was 2.0°C.

9. Dispersion D4

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The inventive dispersion D4 was prepared in analogy to the comparative dispersion CD4.

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Monomer emulsion I: 47.84 g of deionized water
66.50 g of emulsifier solution 3
(see CD3)
66.50 g of emulsifier solution 4
(see CD3)
14.25 g of 10% strength by weight
sodium hydroxide solution
332.03 g of methyl methacrylate
312.55 g of n-butyl acrylate
4.75 g of itaconic acid
9.50 g of a 25% strength by
weight solution of N-(methacryl-
oxyethyl)imidazolidin-2-one in
methyl methacrylate

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Monomer emulsion II: 16.98 g of deionized water
28.50 g of emulsifier solution 3
28.50 g of emulsifier solution 4
108.02 g of methyl methacrylate
140.41 g of n-butyl acrylate
2.38 g of itaconic acid
28.50 g of a 25% strength by
weight solution of N-(methacryl-
oxyethyl)imidazolidin-2-one in
methyl methacrylate.

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10. Dispersion D5

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The inventive dispersion D5 was prepared in analogy to the dispersion D4 except that all of the itaconic acid in the monomer emulsion II was replaced by acrylic acid. The MFT of the dispersion was 10°C.

11. Comparative dispersions CD6, CD7 and dispersion D6

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A polymerization reactor was charged with 200 g of deionized water, 0.1 g of formic acid, 7.5 g of emulsifier solution 4 (see CD3), 1.5 g of stearyl alcohol

and 40 g of monomer emulsion and this initial charge was heated to 85°C under nitrogen. Then, at 85°C, 10 g of initiator solution were introduced into the polymerization reactor. 15 minutes after the addition of initiator the remainder of the monomer emulsion was added over the course of 120 minutes and the remainder of the initiator solution over the course of 135 minutes, these additions to the polymerization reactor beginning simultaneously but taking place by way of separate feeds and still at 85°C. After the end of the addition of initiator the 85°C were maintained for a further 2 h, the batch was cooled to 70°C, and then 0.71 g of a 70% strength by weight aqueous solution of tert-butyl hydroperoxide was introduced into the polymerization reactor. This was followed by the metered addition over 30 minutes at 70°C of 5 g of a 10% strength by weight aqueous solution of hydroxymethanesulfinic acid, as the sodium salt. The dispersion was subsequently cooled to room temperature, 12 g of 10% strength by weight sodium hydroxide solution were added, and the dispersion was filtered through a sieve having a mesh size of 250 μm .

Initiator solution: 1.50 g of sodium peroxodisulfate
100.00 g of deionized water

Monomer emulsion: 120.00 g of deionized water
20.00 g of emulsifier solution 1
(see CD1)
80.00 g of emulsifier solution 4
(see CD3)
26.70 g of 15% strength by weight
aqueous sodium lauryl
sulfate solution
5.00 g of polymerizable acid
(Table 1)
1.00 g of mercaptopropyl-
trimethoxysilane
15.00 g of 50% strength by weight
aqueous acrylamide
solution
200.00 g of styrene
300.00 g of n-butyl acrylate

Table 1

Dispersion	polymerizable acid	SC [% by wt.]	LT [%]
CD6	Acrylic acid	48.9	68
CD7	Methacrylic acid	49.2	72
D6	Itaconic acid	49.7	73

SC = Solids content of the dispersion

LT = Light transmittance of a sample diluted to 0.01% by weight, path length 2.5 cm, relative to water

12. Dispersions CD8, CD9 and D7

The dispersions CD8, CD9 and D7 were prepared in analogy to dispersions CD6, CD7 and D6. The following components were included in the initial charge:

200.00 g of deionized water

12.50 g of emulsifier solution 4 (see CD3)

5.00 g of emulsifier solution 1, 20% strength by weight (see CD1)

37.00 g of monomer emulsion

The monomer emulsion had the following composition:

170.00 g of deionized water

35.00 g of emulsifier solution 1, 20% strength by weight (see CD1)

25.00 g of emulsifier solution 4 (see CD3)

x g polymerizable acid (see Table 2)

y g of 50% strength by weight aqueous acrylamide solution

250.00 g of styrene

250.00 g of n-butyl acrylate

Following the polymerization the dispersion was neutralized to a pH of 7.5 with 10% strength sodium hydroxide solution and filtered through a metal sieve having a mesh size of 250 μm .

Table 2

	Dispersion	polymerizable acid [g]	Acrylamide solution [g]	SC [%]	LT [%]
5	CD8	Methacrylic acid; 13.5	15.0	49.1	65
	CD9	Acrylic acid 13.5	15.0	49.9	68
10	D7	Itaconic acid 5.0	0	49.2	71

SC = Solids content of the dispersion

LT = Light transmittance of a sample diluted to 0.01% by weight, path length 2.5 cm, relative to water

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II. Preparing the formulations of the invention

1. Emulsion paints with a pvc of 46.9%; formulation (I)
(comparative examples C1 to C5, Inventive Examples 1 to 5)

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A vessel was charged with the following constituents:

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105.60 g of water
2.00 g of thickener¹⁾
0.80 g of 2-amino-2-methylpropanol with 5% water
1.00 g of dispersant²⁾
3.40 g of 10% strength by weight aqueous
tetrapotassium pyrophosphate solution
1.70 g of commercial biocide³⁾
3.40 g of commercial defoamer⁴⁾
10.10 g of propylene glycol and
10.10 g of dipropylene glycol n-butyl ether.

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The following constituents were added with stirring:

190.10 g of titanium dioxide pigment⁵⁾
181.60 g of feldspar⁶⁾ and
50.70 g of calcined kaolin⁷⁾

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The constituents were mixed for 20 minutes in a high-speed disperser. Then the following constituents were added with stirring:

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266.01 g of polymer dispersion from I)
2.50 g of commercial defoamer⁴⁾
11.80 g of commercial thickener⁸⁾
159.00 g of water.

The performance properties of the emulsion paints are summarized in Tables 3 and 4.

- 5 2. Solventless interior paint with a pvc of 75%, formulation II (Comparative Examples C6 and C7 and Inventive Example 6)

A vessel was charged with the following constituents:

- 10 106.00 g of water
 1.00 g of 20% strength by weight sodium hydroxide solution
 3.00 g of 35% strength by weight solution of a sodium polyphosphate in water²²⁾
 3.00 g of dispersing auxiliary⁹⁾
 15 3.00 g of preservative¹⁰⁾
 4.00 g of defoamer¹¹⁾
 180.00 g of 2% strength by weight aqueous hydroxyethyl-cellulose solution¹⁾

- 20 The following constituents were added with stirring:

- 65.00 g of titanium dioxide pigment¹²⁾
 5.00 g of aluminum silicate¹³⁾
 215.00 g of calcium carbonate, calcite (about 5 μ m) ¹⁴⁾
 55.00 g of calcium carbonate, precipitated, 0.3 μ m ¹⁵⁾
 25 95.00 g of calcium carbonate, chalk, 2.4 μ m ¹⁶⁾
 65.00 g of talc/dolomite, 6 μ m ¹⁷⁾.

The components were mixed in a disperser, then the following constituents were added with stirring:

- 30 130.00 g of dispersion, 50% by weight, and
 70.00 g of water.

- 35 The solids content of the paint was 57% by weight. The pigment volume concentration was 75%. The performance properties are summarized in Table 5.

- 40 3. Solventborne interior paint with a pvc of 81% formulation III (Comparative Examples C8 and C9 and Inventive Example 7)

A vessel was charged with the following constituents:

- 100.00 g of water
 2.00 g of dispersing auxiliary²⁾
 7.00 g of aqueous solution of a sodium polyphosphate²²⁾
 45 2.00 g of concentrated ammonia solution
 3.00 g of preservative¹⁰⁾

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150.00 g of 2% strength by weight aqueous methyl-
hydroxyethylcellulose solution¹⁸⁾
12.00 g of white spirit K 60¹⁹⁾ and
12.00 g of plasticizer²⁰⁾ .

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The following constituents were added with stirring:

71.00 g of titanium dioxide pigment¹²⁾
12.00 g of aluminum silicate¹³⁾
83.00 g of calcium carbonate, precipitated, 0.3 μm ¹⁵⁾
10 417.00 g of calcium carbonate, calcite 5 μm ¹⁴⁾

The components were mixed with one another in a
high-speed mixer and then the following constituents were
added with stirring:

15 4.00 g of wetting agent²¹⁾
3.00 g of defoamer¹¹⁾
102.00 g of dispersion (50% by weight)
20.00 g of water.

20 The pvc of the paint was 81%. The results of performance
testing are summarized in Table 6.

- 25 1) Hydroxyethylcellulose having a viscosity of 30 Pas
(determined as 2% strength solution in water at
25°C); Natrosol® 250 HR from Hercules GmbH,
Düsseldorf
- 30 2) 30% strength by weight aqueous solution of an
ammonium polyacrylate; Pigmentverteiler [pigment
dispersant] A from BASF AG, Ludwigshafen
- 3) Proxel®GXL from Zeneca GmbH, Frankfurt
- 4) Foammaster®S from Henkel KGaA, Düsseldorf
- 5) Kronos®2101 from Kronos, Houston/Texas
- 6) Minex®4 from Unimin Speciality Minerals Inc.
Elco/Illinois, average particle size 7.5 μm
- 35 7) Icecap® from Burgess Pigment Co., Sandersville,
Georgia
- 8) 20% strength by weight solution of an associatively
thickening polyurethane, Acrysol RM 2020 from Rohm
and Haas Deutschland GmbH, Frankfurt
- 40 9) 35% strength by weight aqueous solution of a sodium
polyacrylate; Pigmentverteiler [pigment dispersant]
NL from BASF AG, Ludwigshafen
- 10) Parmetol®A23 from Schulke & Mayr GmbH, Norderstedt
- 11) Agitan 280 from Münzing-Chemie GmbH, Heilbronn
- 45 12) Kronos®2043 from Kronos Titan GmbH, Leverkusen
- 13) Aluminum silicate P 820 from Degussa AG, Frankfurt

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- 14) Calcite, average particle size 5 μm ; Omyacarb 5GU from Omya GmbH, Cologne
- 15) Socal P2 from Deutsche Solvay GmbH, Solingen.
- 16) Omya Violette Etikette from Omya GmbH, Cologne
- 5 17) Talc/dolomite, average particle size 6 μm ; Naiatsch SE-Micro from Luzenac Deutschland GmbH, Düsseldorf
- 18) MN 20000 GB, Wolff Walsrode GmbH, Walsrode
- 19) Boiling range 180 - 210°C, Esso Chemie GmbH, Cologne.
- 10 20) Diisobutyl ester of a mixture of C₄-C₆ dicarboxylic acids, Lusolvan® FBH, BASF AG
- 21) Lumiten N-OC from BASF AG, 30% strength by weight solution of a fatty alcohol ethoxylate, cloudpoint in aqueous sodium chloride solution: 90°C.
- 22) Calgon® from BK Ladenburg, Ladenburg

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III. Determining the performance properties

1. Abrasion resistance

20 For the formulation I the abrasion resistance was determined in accordance with ASTM D 2486 using a Gardner abrasion machine and a standardized abrasive medium (abrasive type SC-2).

25 The emulsion paints of formulation I were applied with a box-type coating bar (gap height 175 μm , 7 MIL) to Leneta sheets. The sheets were then dried in a climatically controlled chamber for 14 days under standard climatic conditions (23°C, 50% relative atmospheric humidity). The dry coat thickness was about 50 μm .

30 For each emulsion paint the abrasion test was carried out on 3 sheets. For this purpose, a metal strip 250 μm thick was placed underneath the center of the sheet. Abrasive paste was then applied, and abrasion was carried out with a nylon brush until the coating had been abraded right through at the point lying above the metal. The parameter indicated is the number of double strokes required to bring about this complete abrasion at one point. It is stated as the average of two values which deviate by less than 25%.

35 The emulsion paints of formulation II were tested for their abrasion resistance in accordance with DIN 53778 sheet 2: a 60 mm wide coating bar was used to apply a coating film to a Leneta sheet of approximately 430 x 80 mm. The gap height was chosen so as to give a

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dry coat thickness of 100 μm . The film was dried under standard climatic conditions for 28 days. Then an abrasion brush was guided over the coating in an abrasion device with continuous dropwise addition of a 0.25% strength aqueous solution of sodium n-dodecylbenzene-sulfonate. The number of double strokes until the coating was abraded right through was used as the parameter for the wet abrasion resistance.

The emulsion paints from III were likewise tested for their wet abrasion resistance in accordance with DIN 53778. In deviation from the above procedure, however, the formulation was applied in a wet coat thickness of 280 μm . The coating was dried at 50°C for 2 days and then under standard climatic conditions for a further 5 days.

2. Blocking resistance

The blocking resistance was determined in accordance with ASTM D 4946. For this purpose the emulsion paints from II were applied with a box-type coating bar (3 MIL, gap height 75 μm) to Leneta sheets. The sheets were then dried for 24 hours under standard climatic conditions. The dried and coated sheets were subsequently cut into 3.8 cm squares. The squares were placed on top of one another with the coated sides facing and were inserted between two glass plates. A weight of 2 kg was placed on top of these glass plates. This arrangement was stored at 50°C for 24 hours. The sheets were then investigated for their parting behavior. The results were based on a rating scale from 0 to 10:

- 0 = 75 to 100% tearing of the coating
- 1 = 50 to 75% tearing
- 2 = 25 to 50% tearing
- 3 = 5 to 25% tearing
- 4 = very tacky: 0 to 5% tearing;
- 5 = moderate tack
- 6 = slight tack
- 7 = slight to very slight tack
- 8 = very slight tack
- 9 = barely any tack
- 10 = no tack

3. Wet adhesion

The wet adhesion was determined as follows: In a first
 step the Leneta sheets were coated with a solventborne
 alkyd resin lacquer (Glasurit EA, high-gloss lacquer from
 BASF deco GmbH, Cologne) using a box-type coating bar
 (gap height 180 μm). The sheets were dried for 24 hours
 in a standard-climate chamber and then in an oven at 50°C
 for 14 days. The emulsion paints from II were then
 applied to the resin-coated Leneta sheets as a second
 coating, using an applicator (gap height 250 μm , 10 MIL).
 The resulting sheets were dried under standard climatic
 conditions for 3 days. Three test specimens were cut from
 each sheet. Each test specimen was scribed horizontally
 using a razorblade, and then a freeze/thaw test was
 conducted. For this test the specimens were wetted with
 water and subsequently stored in a deep freeze at -20°C
 for 16 hours. This procedure was repeated twice. The
 samples were then allowed to warm to room temperature in
 water. Thereafter, the adhesion of the coating at the
 scribe mark was assessed by scratching with the
 fingernail, on the basis of a rating scale from 0 to 5,
 where 0 denotes optimal adhesion and 5 denotes no
 adhesion (flawless removal). The ratings 1 to 4 denote
 intermediate values.

Table 3: Performance testing of the formulation I
(single-stage polymers)

Example	Disper- sion	Acid ¹⁾ [% by wt.]	MFT ²⁾ [°C]	Blocking resis- tance	Wet adhesion	Wet abrasion resistance
C1	CD1	MAA; 2	6.0	10	2	1200
C2	CD2	IA; 2	4.0	10	2	1000
C3	CD3	IA; 2	2.0	10	3	1325
1	D1	IA; 1	2.0	10	2	2000
2	D2	IA; 1	4.0	10	3	1700
3	D3	IA; 0.75	2.0	10	3	2200

1) % by weight based on the overall weight of the polymer:
MAA = methacrylic acid, IA = itaconic acid

2) minimum film-forming temperature

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Table 4: Performance testing of the formulation I
(two-stage polymers)

Example	Disper- sion	Acid ¹⁾ [% by wt.]	MFT ²⁾ [°C]	Blocking resis- tance	Wet adhesion	Wet abrasion resistance
C4	CD4	AA; 0.75	13.0	9	3	1270
C5	CD5	MAA; 0.75	10.0	10	3	1330
4	D4	IA; 0.75	9.0	10	3	2800
5	D5	IA; 0.5 AA; 0.25	12.0	10	4	2200

1) % by weight, based on the overall weight of the polymer:
AA = acrylic acid, MAA = methacrylic acid, IA = itaconic acid

2) minimum film-forming temperature

Table 5: Performance testing of the formulation II

Example	Dispersion	Acid [% by wt.] ¹⁾	Wet abrasion resistance
C6	CD6	AA; 1	2350
C7	CD7	MAA; 1	2670
6	D6	IA; 1	4660

1) % by weight, based on the overall weight of the polymer:
AA = acrylic acid, MAA = methacrylic acid, IA = itaconic acid

Table 6: Performance testing of the formulation III

Example	Dispersion	Acid [% by wt.] ¹⁾	Amide [% by wt.] ²⁾	Wet abrasion resistance
C8	CD8	MAA; 2.6	AM; 1.4	1320
C9	CD9	AA; 2.6	AM; 1.4	1336
7	D7	IA; 1.0	---	3113

1) % by weight, based on the overall weight of the polymer:
AA = acrylic acid, MAA = methacrylic acid, IA = itaconic acid

2) % by weight, based on the overall weight of the polymer:
AM = acrylamide

ART 34 AMDT

We claim:

1. Emulsion paint comprising

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i) a polymeric binder, which comprises at least one copolymer P of ethylenically unsaturated monomers M in the form of an aqueous polymer dispersion which has a glass transition temperature T_g in the range from -10 to +50°C, and which contains in polymerized form

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a) 0.1 to 1.5% by weight, based on the overall weight of the copolymer P, of itaconic acid as acidic monomer M1, its salt and/or its anhydride, it being possible for up to 50% by weight of the itaconic acid to be replaced by another monomer having at least one acid group or one neutralized acid group,

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b) at least 80% by weight monomers M2, selected from vinylaromatic monomers, the esters of ethylenically unsaturated C_3 - C_8 monocarboxylic acids with C_1 - C_{12} -alcohols, and the vinyl esters of aliphatic C_1 - C_{12} monocarboxylic acids,

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and which contains no polymerized acrolein,

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ii) at least one inorganic pigment,

iii) if desired, inorganic fillers/extenders, and

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iv) customary auxiliaries.

2. A formulation as claimed in claim 1, in which itaconic acid is the sole acidic monomer.

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3. Emulsion paint as claimed in claim 2 in which the monomers M2 are selected from methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, tert-butyl methacrylate, ethyl acrylate, n-butyl acrylate, tert-butyl acrylate and 2-ethylhexyl acrylate.

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4. Emulsion paint as claimed in any one of the preceding claims, in which the monomers M additionally comprise from 0.1 to 10% by weight, based on the overall weight of the copolymer P, of monomers M3 comprising urea groups.

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Claims as amended during International Preliminary Examination

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5. Emulsion paint as claimed in any one of the preceding claims, in which the aqueous dispersion of the copolymer P is obtainable by free-radical aqueous emulsion polymerization of the monomers M in accordance with a monomer feed process
- 5 where at least 50% by weight and in particular all of the itaconic acid is present in the monomer feed.
6. Emulsion paint as claimed in claim 5, in which the free-radical aqueous emulsion polymerization is conducted in at
- 10 least two polymerization stages, where the composition of the monomers to be polymerized in the 1st stage is different from that of the monomer mixture of the monomers to be polymerized in the 2nd stage.
- 15 7. Emulsion paint as claimed in any one of the preceding claims, in which the ratio of inorganic constituents to copolymer P is characterized by a pigment volume concentration pvc > 10%.
8. The use of a copolymer P comprising itaconic acid, as defined
- 20 in any one of claims 1 to 6, for improving the wet abrasion resistance of polymer-bound coating compositions, especially emulsion paints.

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Abstract

The present invention provides pigment-comprising aqueous
5 formulations which comprise

- 10 i) at least one copolymer P of ethylenically unsaturated monomers M in the form of an aqueous polymer dispersion which comprises from 0.1 to 1.5% by weight, based on the overall weight of the copolymer P, of itaconic acid as acidic monomer M1, its salts and/or its anhydride in copolymerized form, it being possible for up to 50% by weight of the itaconic acid to be replaced by another monomer having at least one acid group or one neutralized acid group, and has a glass transition temperature T_g in the range from -10 to +50°C,
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- ii) at least one inorganic pigment,
- iii) if desired, inorganic fillers/extenders, and
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- iv) customary auxiliaries.

The present invention also provides for the use of the copolymers P comprising itaconic acid for improving the wet abrasion
25 resistance of polymer-bound pigmented coating compositions.

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Declaration, Power of Attorney

(9)

Page 1 of 3

0050/048864

We (I), the undersigned inventor(s), hereby declare(s) that:

My residence, post office address and citizenship are as stated below next to my name,

We (I) believe that we are (I am) the original, first, and joint (sole) inventor(s) of the subject matter which is claimed and for which a patent is sought on the invention entitled

Dispersion resins containing itaconic acid for improving wet abrasion resistance

the specification of which

☐ is attached hereto.

☐ was filed on _____ as

Application Serial No. _____

and amended on _____.

☒ was filed as PCT international application

Number PCT/EP 99/ 01690

on March 15, 1999

and was amended under PCT Article 19

on _____ (if applicable).

We (I) hereby state that we (I) have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

We (I) acknowledge the duty to disclose information known to be material to the patentability of this application as defined in Section 1.56 of Title 37 Code of Federal Regulations.

We (I) hereby claim foreign priority benefits under 35 U.S.C. § 119(a)–(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed. Prior Foreign Application(s)

Application No.	Country	Day/Month/Year	Priority Claimed
19811314.5	Germany	16 March 1998	<input checked="" type="checkbox"/> Yes <input type="checkbox"/> No

We (I) hereby claim the benefit under Title 35, United States Codes, § 119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

(Application Number)

(Filing Date)

We (I) hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

Application Serial No.

Filing Date

Status (pending, patented,
abandoned)

_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

And we (I) hereby appoint:

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10
_____, our (my) attorneys, with full powers of substitution and revocation, to prosecute this application and to transact all business in the Patent Office connected therewith; and we (I) hereby request that all correspondence regarding this application be sent to the firm of **OBLON, SPIVAK, MCCLELLAND, MAIER & NEUSTADT, P. C.**, whose Post Office Address is: Fourth Floor, 1755 Jefferson Davis Highway, Arlington, Virginia 22202.

We (I) declare that all statements made herein of our (my) own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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